REFRACTORIES FOR THE GLASS INDUSTRY

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INVESTIGATION OF REFRACTORY CONCRETE MATERIALS WITH ALUMOSILICATE COMPOSITION BY PETROGRAPHIC METHODS

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Petrographic methods are used to investigate concrete alumosilicate materials, produced by the Semiluki Refractory Works, on fireclay fill and an integral binder based on high-alumina cement. The microscopic investigations showed that as the result of heat treatment of concrete up to 380°C degradation processes are essentially completed in the binding substance, and formation of a glass phase, mullitization, and binder penetration into the fireclay fill are observed in samples calcined at 1000°C. After calcination the phase composition of the binder obtained from synthetic materials is similar to the composition of the clay binder used in conventional fireclay calcination materials.

Alumosilicate fireclay refractories (the system Al_2O_3 – SiO_2) are usually obtained by high temperature calcination of a grainy mixture of precalcined refractory clay or kaolin (fireclay) and plastic refractory clay. Most kaolins and refractory clays are kaolinite rocks whose main mineral component is hydrated silicon dioxide alumina — kaolinite and minerals come close to it, with the general formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ [1, 2].

Investigation of the solid phase of fireclay refractories showed that it consists of a mixture of mullite $3Al_2O_3 \cdot 2SiO_2$ and crystalline modifications of silica — cristobalite, tridimite, and quartz — products of the thermal regeneration of kaolinite in the process of technological calcination of the refractory [3]:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{400\,-\,600^\circ C} Al_2O_3 \cdot 2SiO_2 + 2H_2O\uparrow;$$

$$3[Al_2O_3 \cdot 2SiO_2] \xrightarrow{>1200^\circ C} 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2.$$

The formation of the phase composition of fireclay material in the calcination process can be represented as follows.

The kaolinite of the clay binder decomposes, on heating to 500 – 600°C, with chemically bound water being released and after dehydration it exists, in the opinion of a number of investigators, in the form of the metakaolinite Al_2O_3 – $2SiO_2$ up to the optimum temperature 800 – 900°C [1] or it decomposes on dehydration into Al_2O_3 and SiO_2, present in a state of interpenetration [2].

At a temperature of about 920 – 940°C polymorphic transformations of amorphous alumina and formation of hidden crystalline mullite occur. At higher temperatures calcination of material begins as result of the appearance of a liquid phase (as a result the melting of the low-melting impurity minerals) and the interaction of impurities with the decomposition products of kaolinite — silica and alumina. At the same time, needle-shaped crystals of mullite grow and amorphous silica which is not bound in mullite transforms into cristobalite.

The final calcination temperature of fireclay refractories usually is in the range 1350 – 1400°C. At this temperature the crystallization of mullite in the form of individual crystals 2 – 5 μm in size is completed and their clusters in a glassy, weakly crystallized (amorphous), substance containing silica and a negligible amount of flux. This is, in fact, the binding substance of conventional fireclay refractories.

Fireclay refractory articles contain 35 – 50% mullite and 50 – 60% (by volume) and alumosilicate glass. Mullite is the predominant mineral and the carrier of the main properties of the refractory [4].

Unlike conventional refractories, concrete articles belong to the class of heat-worked refractories. The final temperature of their heat treatment, as a rule, does not exceed 800°C. Modern concrete articles are fabricated by vibrational casting from thixotropic pastes, whose main components are

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coarse fill and a complex, finely dispersed, binding system based on high-alumina cement (matrix) [5].

The matrix of refractory concrete is a complex multi-component system consisting of ultradispersed powders and various inorganic and organic reagents which regulate the rheological properties of the mixture. It is necessary to know the phase composition of the binder, since it forms mainly when the thermal aggregate is heated up to the operating temperature and determines the defect-free service of noncalcined refractory. By selecting the optimal composition of the matrix and determining the regime for primary heat treatment of a concrete part as well as the correct schedule for raising the temperature when the furnace is heated up to the working temperatures the refractory will have the physical-mechanical and operating characteristics, which satisfy the conditions for operation of a thermal aggregate, without preliminary high-temperature calcination.

Aside from the phase components, i.e., the chemical-mineral composition of the refractory, the microstructure of the refractory has a large effect on the properties and technological characteristics of refractory concretes — the character of the development and spatial interrelation of the phases: at first gel and crystals, after calcination crystals and glass; well-formed crystals (plates, prisons, needles, rounded grains), determining the physical-mechanical properties of the material. The character of the porosity, the degree of uniformity of the paste, foreign inclusions, and so forth can all be determined using petrographic analysis, which provides an accurate orientation for the phase composition of the overwhelming majority of refractory materials when studying their structure.

The present article examines the results of petrographic investigations of refractory materials, performed using the POLAM-R-211 optical polarization microscope (in transmitted light and with crossed polaroids) for the purpose of studying the interference coloration of the components of concretes. Sections were prepared using the epoxy resin Done dial with index of refraction about 1.545 as the binder. Refractory concrete materials based on fireclay fill with a complex binder of hydration hardening based on high-alumina cement were investigated. Articles made from such materials are produced by the Semiluki Refractory Works and are used as the bottom bars of glass-making furnaces. A modification of the material was also developed for use as a bottom bar for the lining of a tin melt pool without preliminary high-temperature calcination.

Samples of calcined fireclay bottom bars produced by Saratovstroisteklo (Saratov Technical Glass Works), which are used for lining the bottom of the tin melt pool and obtained by the method of tamping followed by high temperature calcination, as well as data from petrographic investigations were used for comparison [6].

To develop refractories for the domestic two-stage method for obtaining polished glass, petrographic investigations of alumosilicate refractories with corundum, corundum-mullite, sillimanite, kaolin, and fireclay compositions,

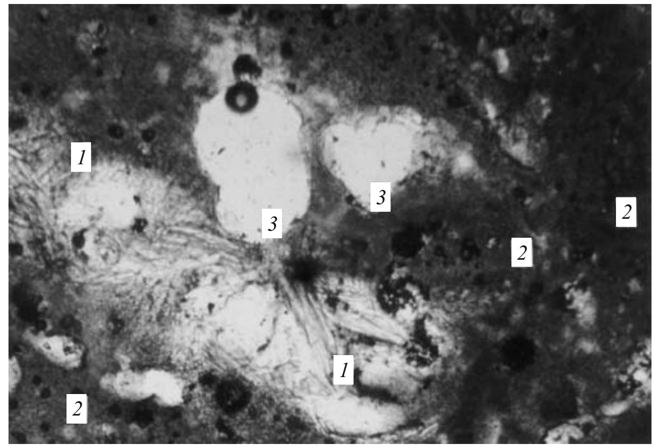

Fig. 1. Saratov fireclay bottom bar for a tin melt pool, calcination temperature 1325 – 1350°C (× 150, polaroids //). Formation of needle – prism shaped crystals of mullite (*1*) between fireclay fragments (*2*), large pores are seen (*3*), and kyanite-sillimanite crystals are encountered.

which after annealing were subjected to testing in the temperature interval 600 – 1000°C, were conducted at the Saratov Glass Institute. The investigations showed that the special tamped calcined fireclay refractory for the lining of a tin melt pool consists of fireclay fragments up to 3 – 4 mm in size, individual grains of quartz, and binder paste. The fireclay fragments and binder consist of slightly crystallized mullitized material. In a reductive atmosphere at 1000°C, mineralogical changes do not occur in the refractory; mullite is released, the main mass of the material is compacted, and the porosity decreases by 2 – 3%. In fireclay fragments, a glassy phase and separate, round, closed pores are formed, and better crystallization of mullite from melt is noted [6].

Such fireclay articles (in what follows — Saratov bottom bar) have served for decades in the tin melt pools of domestic production lines and, for this reason, can be used as an example for comparing with the concrete materials being developed.

Fragments of kaolin fireclay with an oriented, and less often disordered, fibrous structure forming in it a slightly crystallized mullite, which do not lie flush against one another are observed in the sections of the Saratov bottom bar which were investigated in the present work. The fireclay contains 10 – 70% white opaque particles, less than 0.01 mm in size, distributed uniformly as well as a glassy phase and cristobalite (determined in thin parts of a section at the edges of pores). In some sections between fragments of kaolin fireclay, large needle – prism shaped crystals of transparent mullite up to 0.2 – 0.4 mm long, which form interpenetrating nodules, grow in some sections between fragments of the kaolin fireclay; kyanite and sillimanite crystals are rarely seen (Fig. 1).

Microscopic investigations of samples of concrete produced at the Semiluki works (in what follows — Semiluki concrete bar) were performed after several successive stages

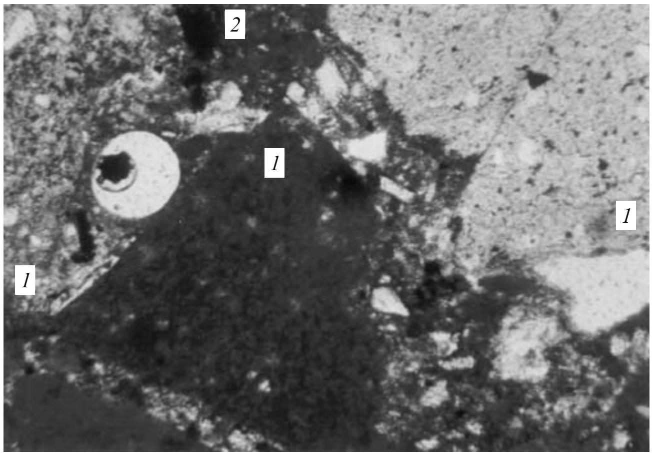

Fig. 2. Semiluki concrete bar, heat treatment at 110°C (× 150, polaroids //). The binder (*2*) lies flush against the filler (*1*).

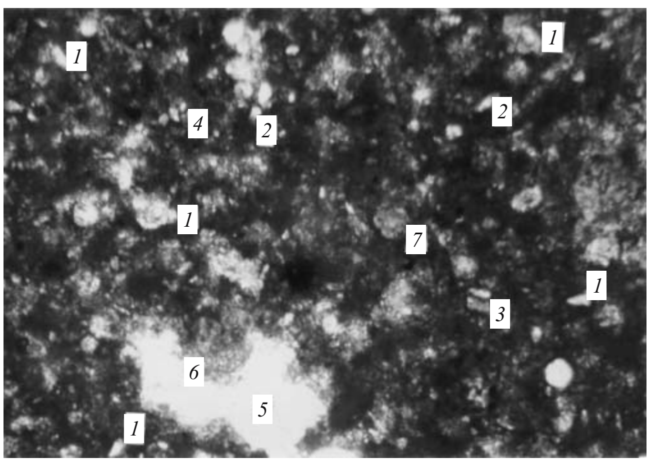

Fig. 3. Semiluki concrete bar, heat treatment at 380°C (× 150, polaroids //). The general structure of the binder: calcium aluminates (*1*, *2*) and kyanite-sillimanite (*3*, *4*) are observed against the background of a finely dispersed phase; a hidden crystalline structure of cristobalite (*6*) can be distinguished along the contour of pores (*5*); an iron glass phase (*7*) is encountered.

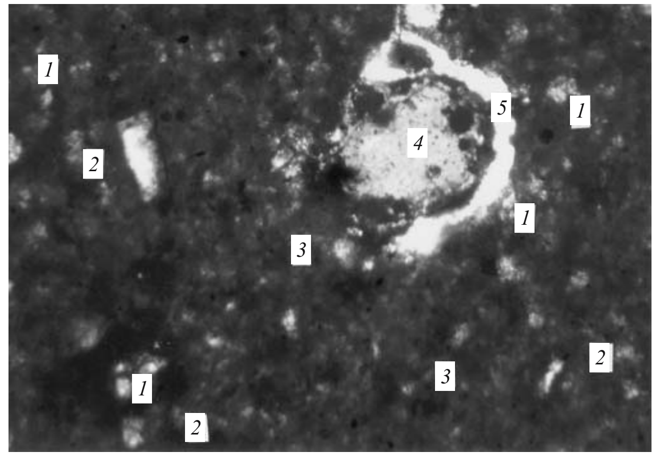

Fig. 4. Semiluki concrete bar, heat treatment at 1000°C (× 150, polaroids //). Melted calcium aluminates (*1*, *2*), mullite (*3*), and a glassy formation (*4*) in a pore (*5*).

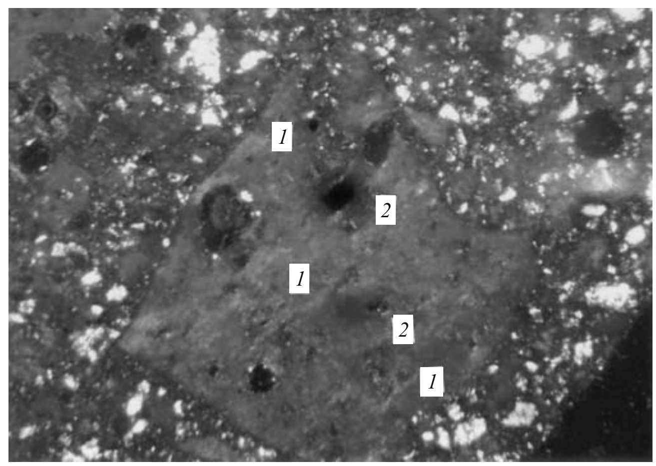

Fig. 5. Semiluki concrete bar, heat treatment at 1000°C (× 150, polaroids //). Structure of the binder: a bright white interference color of calcium aluminates is observed (*1*), new formations of mullite (*2*) and pores are present.

of heat treatment in order to determine the stages of structure formation in the material. A structure characteristic of concretes is observed in the samples after drying at 110°C: the binder lies flush against fireclay fragments and comprises about 30 – 35% of the volume (Fig. 2). It contains transparent grains — both single-crystalline and within aggregate structure. The base consists of finely milled fireclay and finely dispersed, almost isotropic, alumina substance, and quartz and hydrated calcium aluminate are present in the mass of particles.

The structure of the binder of the material heat-treated at 380°C is very fine. Individual crystalline formations are distinguished only in the thinner areas of the section. Particles of calcium aluminates and kyanite – sillimanite have sizes in the range 0.01 – 0.02 mm (Fig. 3), and a certain amount of epidote and an iron glass phase are present.

In sections of samples calcined at 1000°C the contours of closely touching, almost opaque, particles 0.01 – 0.03 mm in size are distinguished with difficulty; up to 50% of these particles are probably mullite (Fig. 4). Hidden crystalline cristobalite and a glassy phase are seen in thin parts of a section.

The binder penetrates into the fireclay along the contour and activates the formation of mullite crystals (Fig. 5). Growth of calcium aluminate crystals, formation of mullite, and enlargement of cristobalite crystals as compared with a sample of the same material but heat-treated at 380°C are observed.

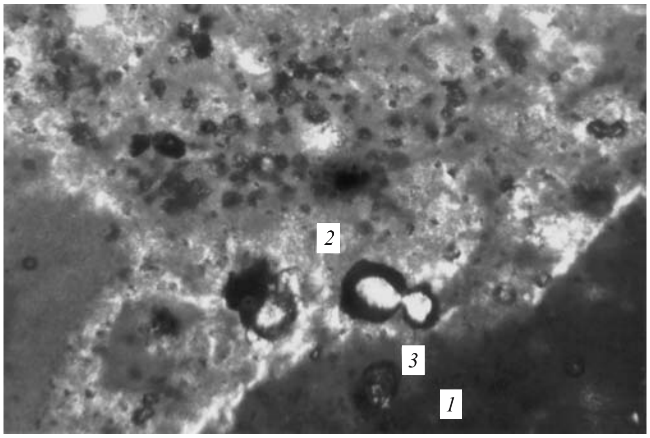

Fig. 6. Semiluki concrete bar, heat treatment at 1400°C (× 150, polaroids //). Dissolution of calcium aluminate crystals (*1*, *2*) with formation of mullite (*3*).

It is known that on melting the chemical potentials of molecules which are in a solid-state and a liquid phase are the same. The increment to the chemical potential of molecules present on the surface of pores is large and results in some cases in an appreciable (by 150°C) decrease of the melting temperature of the solid part adjoining a pore. This gives rise to a liquid phase in the porous solid at temperatures which do not reach the melting point of a compact solid [7], which is observed in the concrete sample calcined up to temperature 1000°C.

The following is observed in a sample of concrete calcined at 1400°C (Fig. 6). The fireclay actively reacts with the binder, the binder penetrates into the fireclay, mullite fibers grow into the binder, and small fragments dissolve completely in it. Neighboring fragments of fireclay sometimes form common intergrowing fields. Dissolution or melting of calcium aluminates and all other aggregates is observed in the binder together with crystallization of needle-fibrous mullite aggregates and separation of fine-crystalline cristobalite. Micrograin quartz forms from cristobalite locally. Glass is formed, in some places yellow and brown iron hydroxides.

A sample of the concrete material Verral, intended for the lining of a tin melt pool, was investigated for comparison as a foreign analogue.

The binder contains semi-dissolved calcium aluminates, immersed in a fine opaque dispersed white substance. Finely milled kaolin fireclay with clusters of micrograin quartz is observed. The fireclay is not compacted and is freely positioned; the binder does not lie flush against the fireclay fragments. Large needle shaped pores are observed. Single epidote-like crystals of calcium aluminates are present. This indicates that the material was calcined at a temperature of 1000°C or below.

In summary, the investigations of the Semiluki concrete materials based on fireclay filler and an integral binder with high-alumina cement have shown that as a result of heat treatment of an article up to 380°C dehydration processes occur in practice in the binding substance and with further heating up to 1000°C a glass phase forms, mullitization occurs, and binder penetrates into the fireclay filler. The phase composition of the binder, which was obtained from synthetic materials, in the concretes from the Semiluki works is similar to the clay binder of classical fireclay calcination materials and it is also similar to foreign concrete.

The results of microscopic investigations of the structure of the binder in concrete samples show that it is possible to use non-calcination concrete articles in the lining of thermal aggregates to obtain glass, including a float pool, provided that the operating temperature regime is reached correctly.

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